REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*

2. REPORT TYPE
Technical Papers

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
2303

5e. TASK NUMBER
M2C8

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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5 Pollux Drive
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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

1121 034

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

a. REPORT	b. ABSTRACT	c. THIS PAGE
Unclassified	Unclassified	Unclassified

17. LIMITATION OF ABSTRACT
A

18. NUMBER OF PAGES

19a. NAME OF RESPONSIBLE PERSON
Leilani Richardson

19b. TELEPHONE NUMBER *(include area code)*
(661) 275-5015

62 separate items are enclosed

TP-FY99-Ø1Ø9

ERC#? (no letter)

✓ Spreadsheet
✓ DTS

MEMORANDUM FOR PRR (Contractor/In-House Publication)

FROM: PROI (TI) (STINFO) 27 May 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-FY99-~~0115~~** 0109 nac
Drake et al., "New Energetic Salts for Monopropellants"
HEDM CONFERENCE **(Public Release)**

New Energetic Salts for Monopropellants

June 9, 1999

U.S. Air Force High Energy Density Materials Meeting

Greg Drake, Adam Brand, Milton McKay, Ismail Ismail*, Tom Hawkins

Propulsion Directorate and *ERC, inc.
Air Force Research Laboratory, Edwards AFB, CA 93524

Overview of Talk

I. Introduction

II. 2-Hydroxyethylhydrazine salts

III. Dimethyltriazanium salts revisited

IV. A look at energetic nitrocyanamide salts

V. Summary, Conclusions, and Outlook

Hydrazine (N_2H_4) is currently the state of the art monopropellant

Problems: **Extreme vapor and dermal toxicity**
Relatively high vapor pressure at ambient temperature (12 torr)
Leads to very high handling and loading costs
Density (1.0 g/cm^3) and performance aren't that spectacular

Another candidate receiving renewed attention is hydrogen peroxide (H_2O_2)
Notorious history of violent decomposition
Incompatible with many materials especially organics and metals

Objective: **To find safer, higher performing monopropellant materials for eventual replacement of hydrazine**

At AFRL, we have been exploring energetic salts as possible new monopropellant materials. Several advantages including significantly higher densities and little or no vapor pressure at ambient conditions.

2-hydroxyethylhydrazine, [$HO-CH_2-CH_2-NH-NH_2$] extensively used in the agricultural field in the 60's and 70's as a flowering agent, especially in pineapple plants.

"Use of reduced volatility substituted hydrazine compounds in liquid propellants", U. S. Patent # 5,433,802, Rothgery, E. F. ; Knollmeuller, K. O. ; Manke, S. E. ; Migliaro, F. W. (1995)

"Monopropellant Aqueous Hydroxy Ammonium Nitrate/Fuel" U. S. Patent # 5,233,057, Mueller, K. F,; Cziesla, M. F. (1993)

"Catalytic Decomposition of Hydroxylammonium Nitrate-Based Monopropellants", U. S. Patent # 5,484,722, Schmidt, E.W.; Gavin, D.F. (1996)

Liquid to low temperatures with no real freezing point to –50°C

Very low vapor pressures at room temperature.

Could salts of this form new monopropellant ingredients?

2-hydroxyethylhydrazinium nitrate (HEHN) from the simple reaction of HEH with concentrated HNO_3

$$HO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}NH_2 + HNO_3\ (aq.) \longrightarrow [HO\text{-}CH_2\text{-}CH_2\text{-}N_2H_4^+]\ [NO_3^-]$$

"HEHN"

viscous liquid at RT
great physical properties, f.p. = -50°C, density = 1.42 g/cm
H_f (calc.) : -107 kcal/mol
Impact sensitivity: 38 kg·cm (5 negatives)
Friction: 9 kg (5 negatives)
class 1.3 explosive
patent applied for by A. Brand and T. Hawkins

HEH mononitroformate $[HO\text{-}CH_2\text{-}CH_2\text{-}N_2H_4^+][C(NO_2)_3^-]$ "HEHNF"

$$HO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}NH_2 + H\text{-}C(NO_2)_3 \longrightarrow [HO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}NH_3^+][C[NO_2)_3^-]$$

"HEHNF"

Viscous yellow oil with significant vapor pressure
Decomposes slowly at RT(gasses), turns dark with bubbles
Can be detonated with a strong hammer blow
DSC studies large exotherm beginning at 75°C with pan exploding

HEH monodinitramide $[HO\text{-}CH_2\text{-}CH_2\text{-}N_2H_4^+][N(NO_2)_2^-]$

Carried out in a strong acid cation exchange resin, using MeOH as the solvent

$$HO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}NH_2 + \text{"}H\text{-}N(NO_2)_2\text{"} \longrightarrow [HO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}NH_3^+][N[NO_2)_2^-]$$

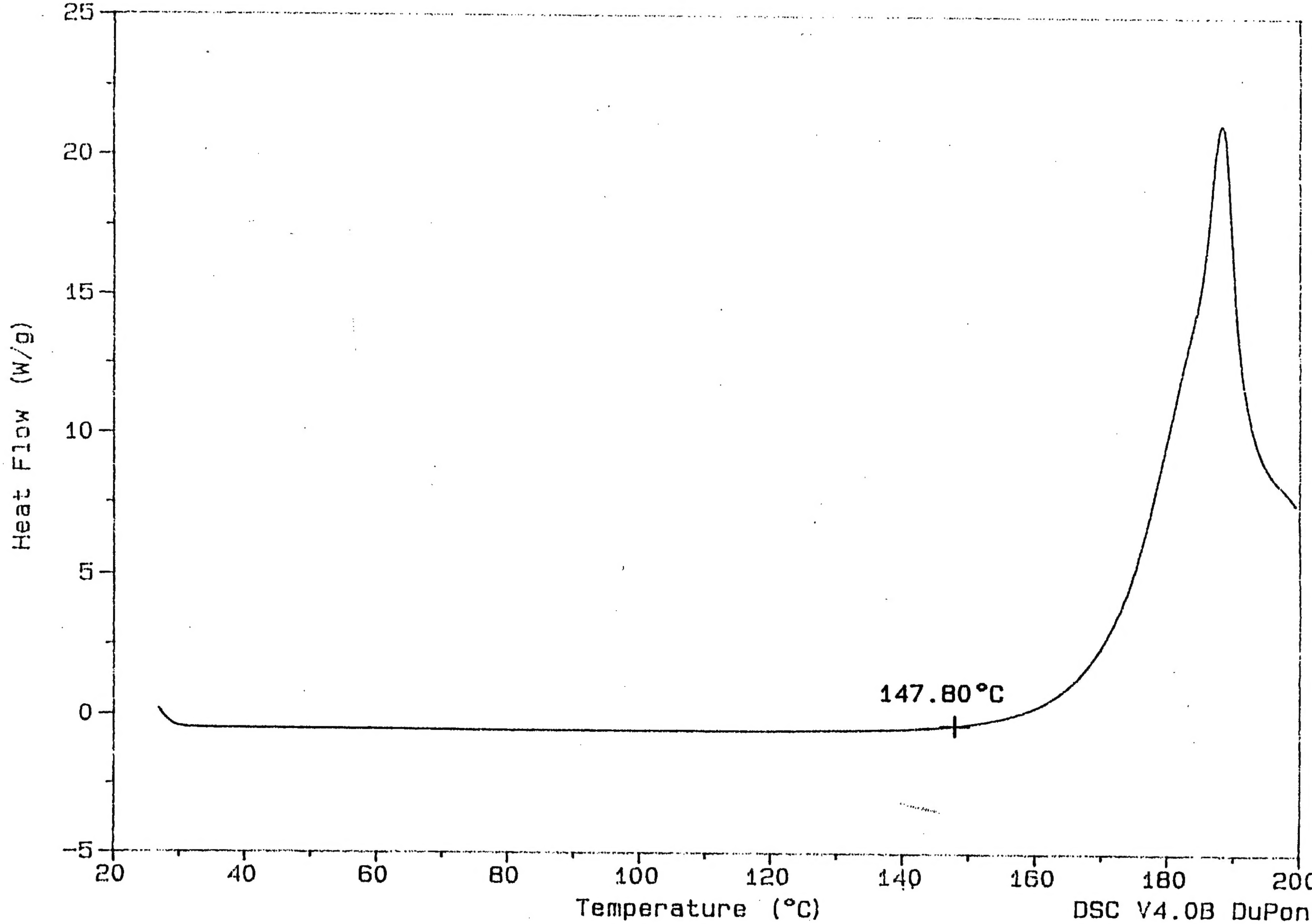
"HEHDNA"

Straw-colored viscous liquid which discolors upon long exposures to light
DSC studies: revealed no decomposition below 150°C
Impact: 5 negatives at 5 kg·cm
Friction: 5 negatives at 112 Newtons
Thermal stability at 75°C: decent, losing only 1.2% per day

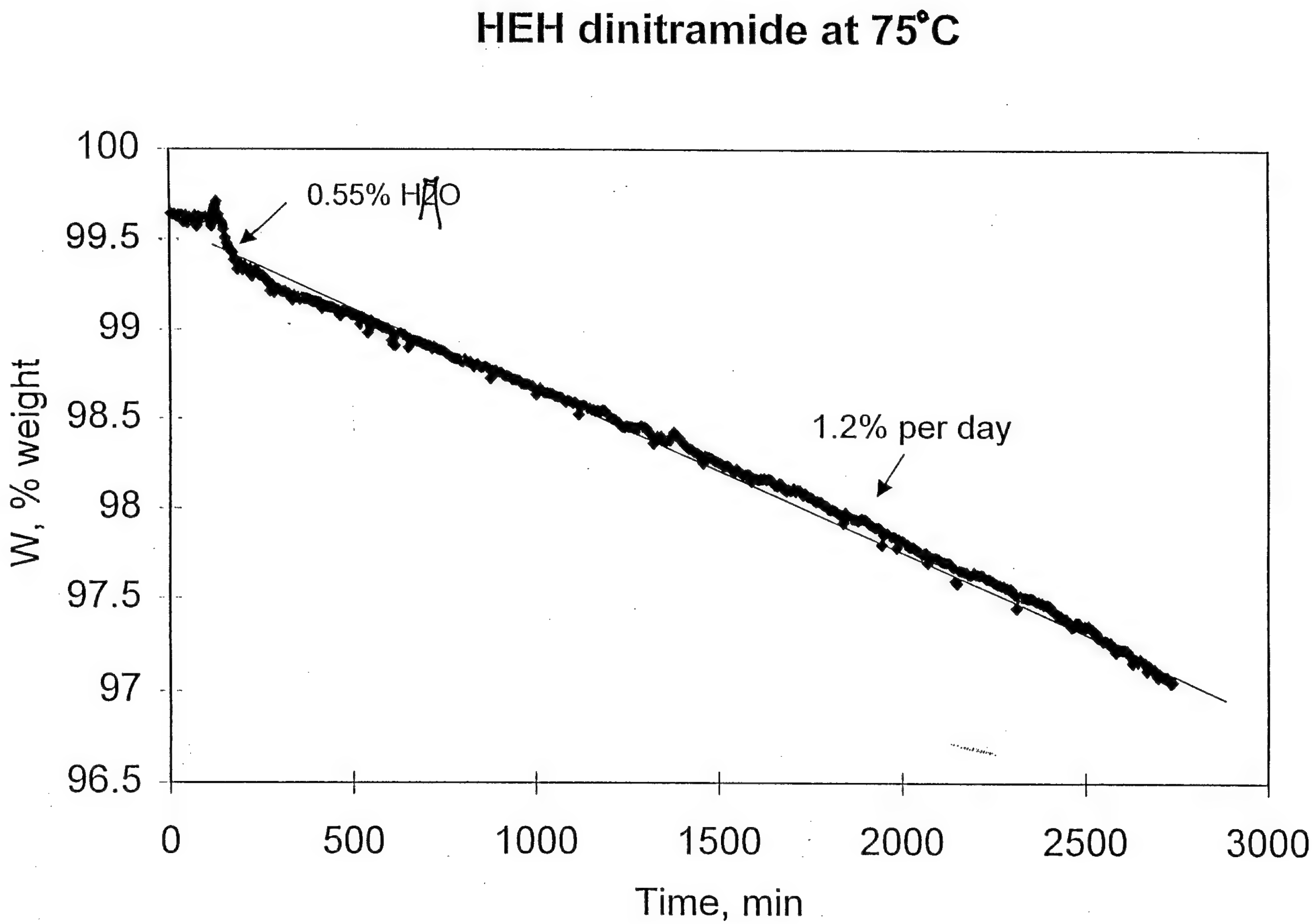
Sample: HEHDNA 1:1 STRAW OIL
Size: 2.0000 mg
Method: PROPELLANTS
Comment: Rate 10°C/MIN, SEALED (CTD) AL PANS IN DRYBOX/ N2 FLOW

DSC

File: C:DRAKE.059
Operator: DRAKE
Run Date: 4-Jun-98 02:41



DSC V4.0B DuPont 2100


HEH dinitramide at 75°C
0.55% H2O
1.2% per day
W, % weight
100
99.5
99
98.5
98
97.5
97
96.5
0
500
1000
1500
2000
2500
3000
Time, min

HEH dinitrate $[HO\text{-}CH_2\text{-}CH_2\text{-}NH_2NH_3^{+2}][NO_3^-]_2$

$$HO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}NH_2 + 2\ HNO_3\ (aq) \longrightarrow [HO\text{-}CH_2\text{-}CH_2\text{-}N_2H_5^{+2}]\ [NO_3^-]_2$$

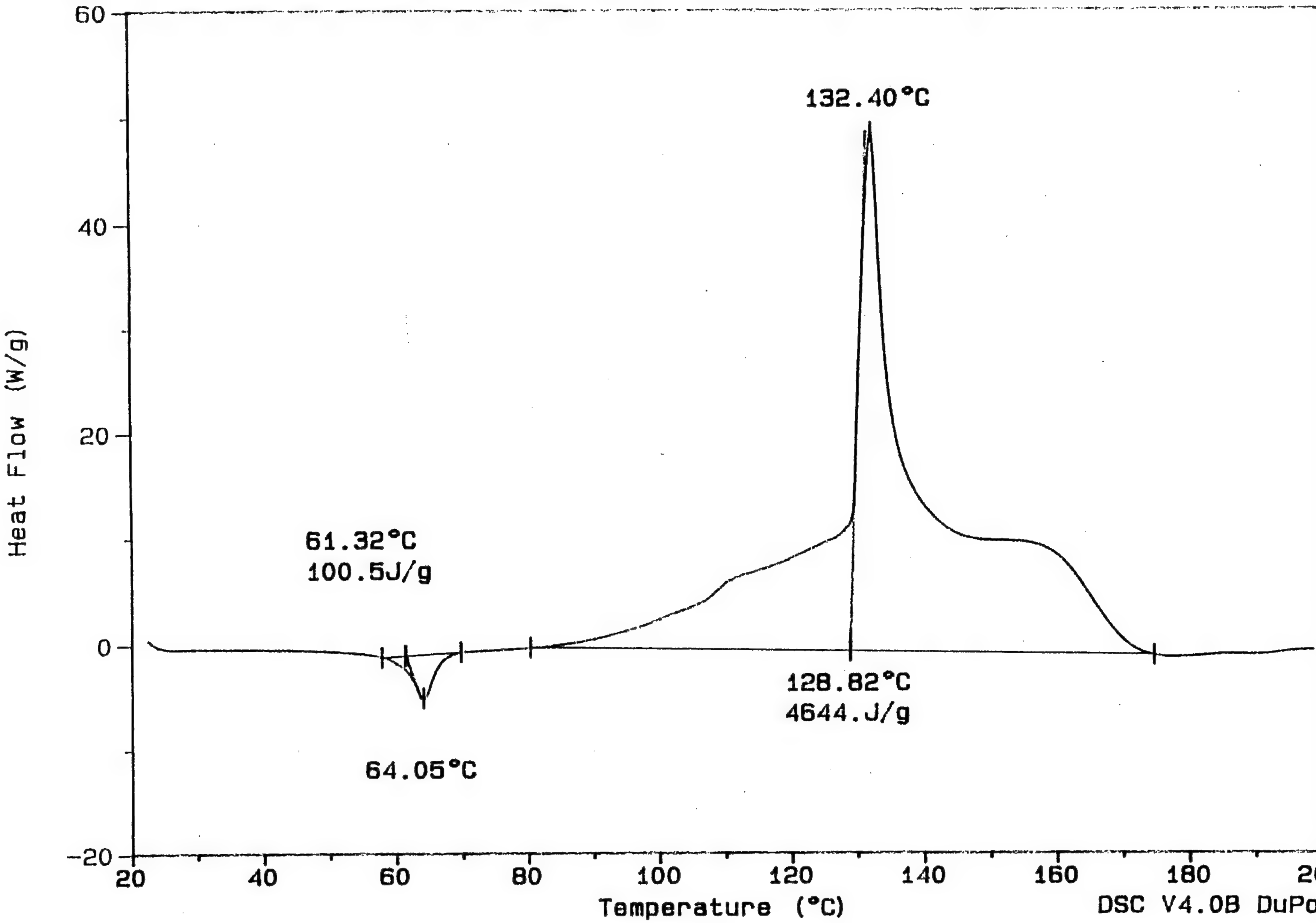
"HEHDN"

White crystalline solid, m.p. 61°C
Density (g/cm^3) : 1.78 (calc.); 1.77 $\pm$0.03 (expt.)
Impact sensitivity: 30 kg-cm
Friction: 12kg
DSC studies: Slow decomp. starting at 110 °C
Thermal properties: very poor losing 40% in first 3hrs at 75°C
H_f (kcal/mol) = -107 (calc.)

Sample: HYDROXYETHYLHYDRAZINE DINITRATE
Size: 1.0000 mg
Method: PROPELLANTS
Comment: 10°C/MIN, Coated Pans, N2 50 ML/MIN

DSC

File: A: DRAKE.040
Operator: gwdpjd
Run Date: 27-Mar-98 06: 06



DSC V4.0B DuPont 2000

HEH diperchlorate $[HO\text{-}CH_2\text{-}CH_2\text{-}NH_2NH_3^{+2}][ClO_4^-]_2$

$HO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}NH_2 + 2\ HClO_4\ (aq) \longrightarrow [HO\text{-}CH_2\text{-}CH_2\text{-}N_2H_5^{+2}]\ [ClO_4^-]_2$

"HEHDP"

White solid, mp 110 °C
Density(g/cm^3) : 2.09 (calc.)
Impact sensitivity: << 10 kg cm
Friction : < 1 kg
Extremely sensitive to both friction and impact, destroyed testing cup and anvil. Friction completely destroyed ceramic plate on lowest setting.
DSC : surprisingly stable with no decomposition until 130 °C
H_f(kcal/mol) : -117 (calc.)
Thermal stability at 75 °C: > 1% per day

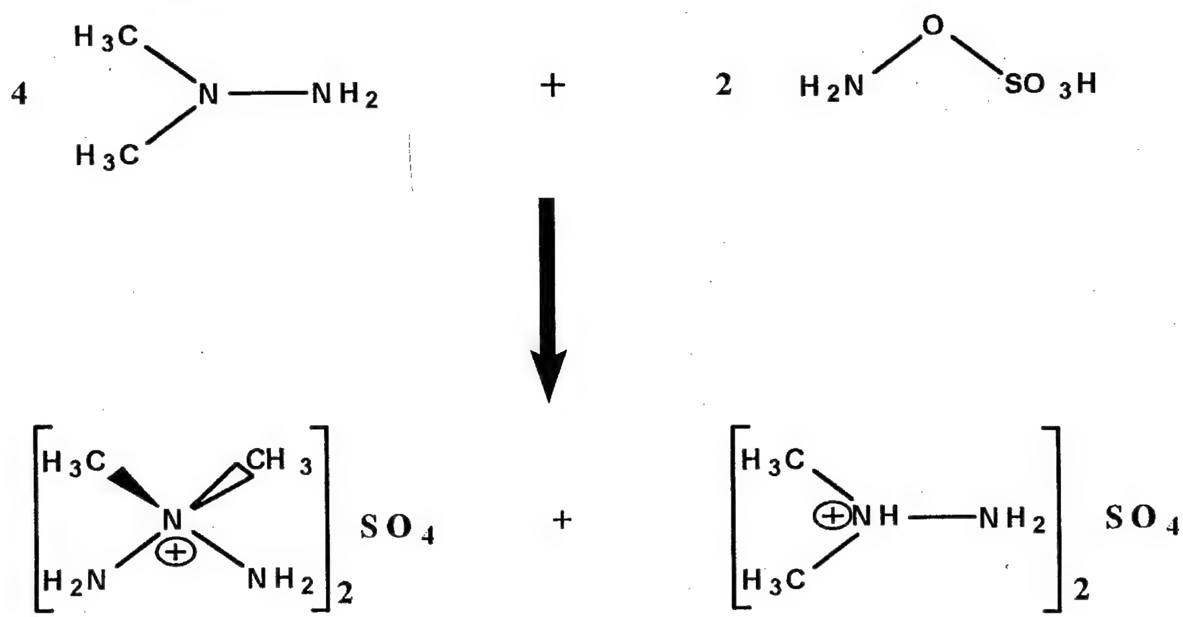
Performance Estimates of "HEHDN" and "HEHDP" versus some known explosive materials

Compound	Density(g/cm^3)	Detonation Velocity (m/sec)	Heat of explosion (kcal/kg)
PETN	1.76	8400	1421
RDX	1.82	8750	1375
HMX	1.85	9100	1357
Nitroglycerine	1.59	7600	1617
Lead azide	4.8	5300	367
Lead styphnate	3.0	5200	370
HEHDN	1.78	8370	1077
HEHDP	2.09	9150	1270

HEHDN and HEHDP compare very well to known materials.

The Dimethyltriazanium cation $[H_2N\text{-}N(CH_3)_2\text{-}NH_2]^+$

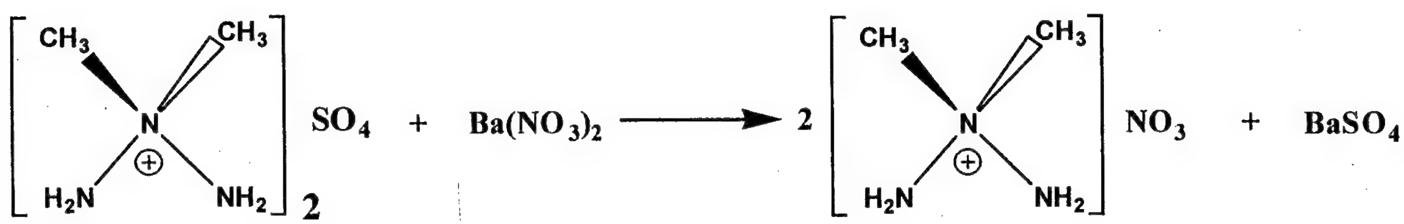
Stable catenated nitrogen chain of 3 nitrogen atoms
First prepared by Goesl in 1962 as the sulfate salt
in a straightforward reaction:



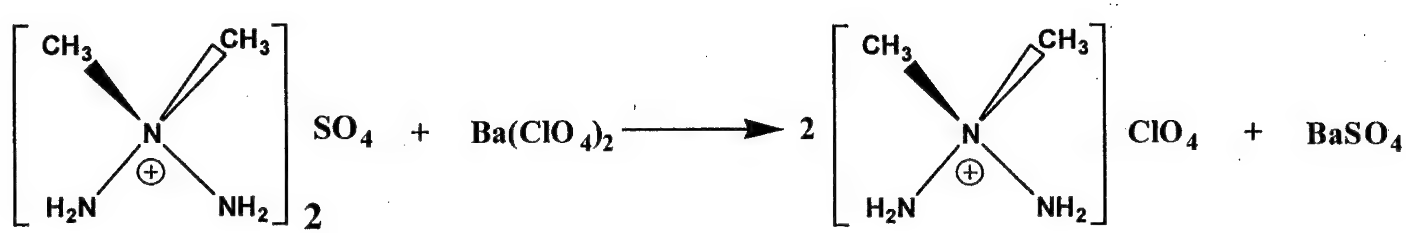
Goesl, R. Angew. Chem Int. Ed. Engl. 1962, *1*, 405.

Energetic salts are made in a straightforward manner, following the synthesis route used by a Rocketdyne chemist[1], and later by Soviet workers[2]

Nitrate salt:



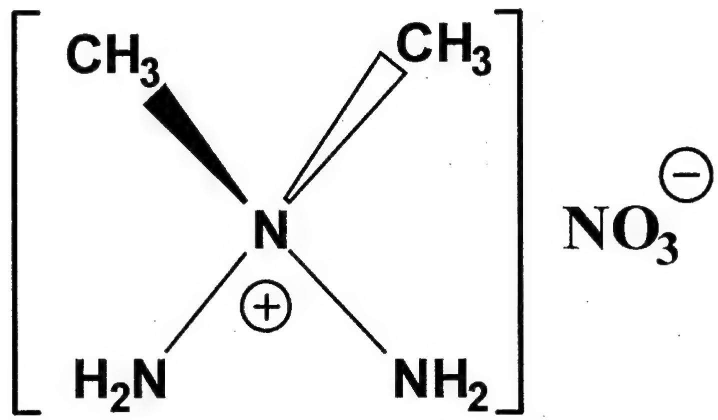
Perchlorate salt:



[1] Grant, L. R. "Chemistry of Catenated Nitrogen Compounds" Rocketdyne Final Report April 1972, Contract # N0019-71-C-0374.

[2] Matyushin, Y. N.; Kon'kova, T. S.; Vorob'ev, A. B.; Loginova, E. N.; Titova, K.V.; Lebedev, Y. A. Izv. Akad. Nauk SSSR 1981, 1735.

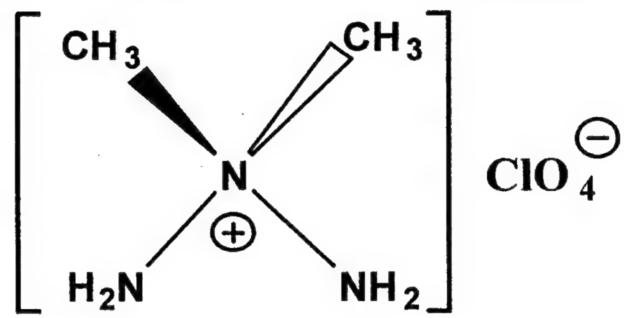
Dimethyltriazanium nitrate



White crystalline solid
Melting point: 134°C
H_f = -34.8 kcal/mole (Russian work)*
DSC: large exotherm after melt
Impact sensitivity: 17 kgcm (5 negatives)
Friction sensitivity: 9 kg (89 newtons)
Thermal stability at 75°C: Very poor

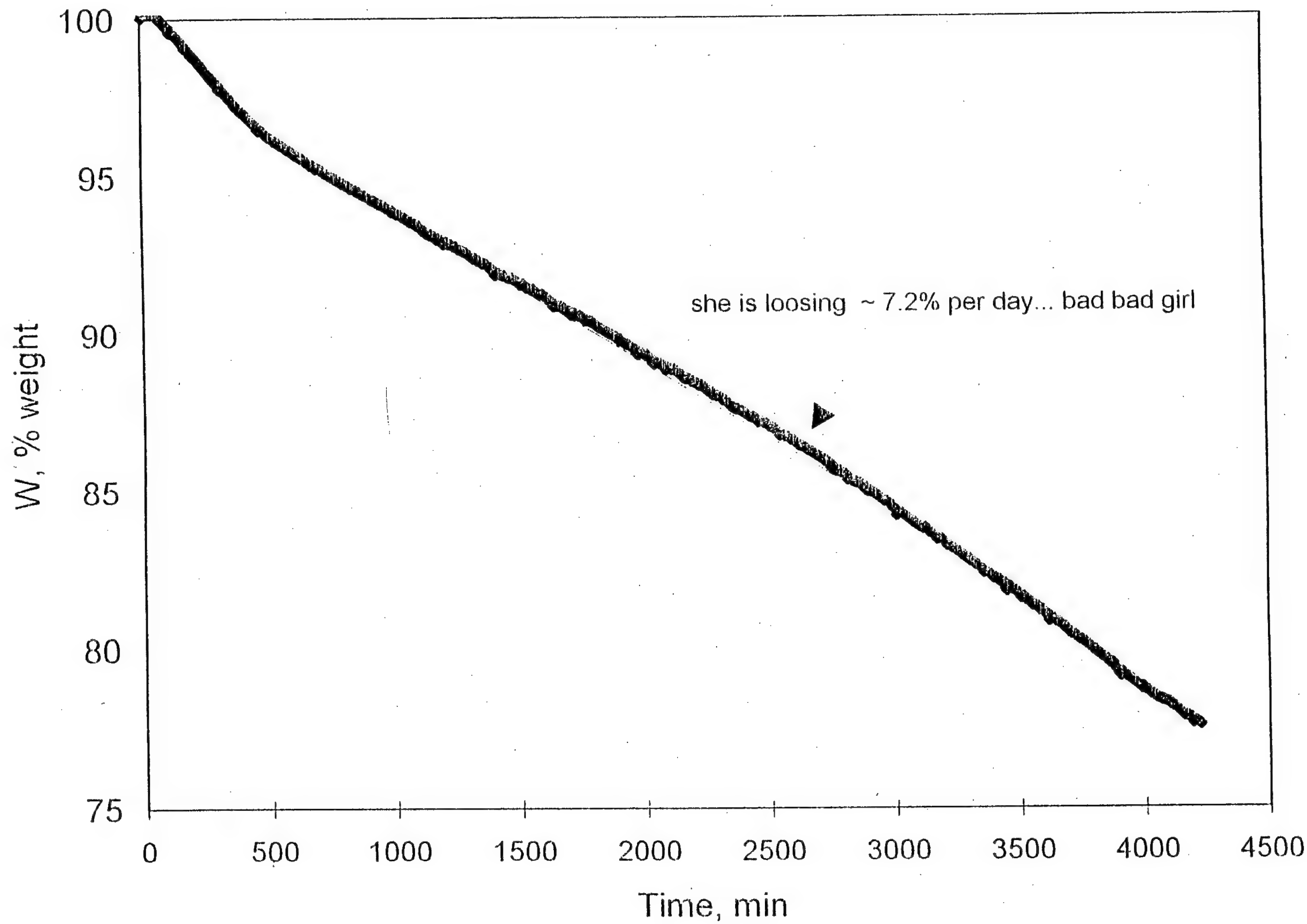
Rubstov, Y. L.; Andrienko L. P.; Titova, K. V.; Loginova, E.N. Izv. Akad. Nauk SSSR Ser. Khim. 1982, 1953

Dimethyltriazanium Perchlorate



White crystalline solid
Melting point: 185°C
H_f = -16.6 kcal/mole*
DSC: exothermic decomposition occurring right after melt
Impact sensitivity: Rather sensitive, 6 kgcm
Friction sensitivity: < 0.5 kg, detonates very easily with pressure
Thermal stability at 75°C: very poor

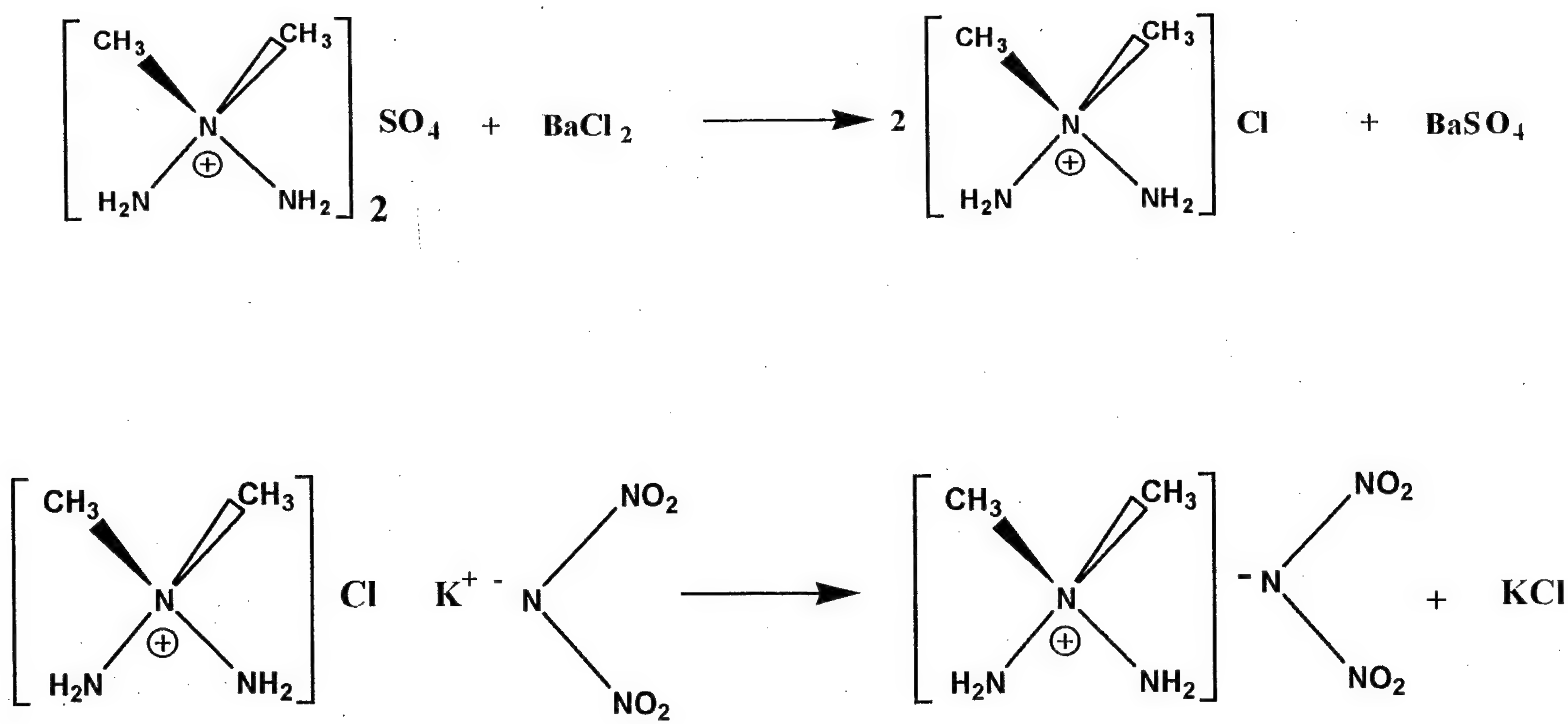
Matyushin, Y. N.; Kon'kova, T. S.; Vorob'ev; Loginova, E.N.; Titova, K. V.; Lebedev, Y. A. Izv. Akad. Nauk SSSR 1981, 1735.



100
95
90
85
80
75
W, % weight
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Time, min
she is loosing ~ 7.2% per day... bad bad girl

Dimethyltriazanium dinitramide synthesis

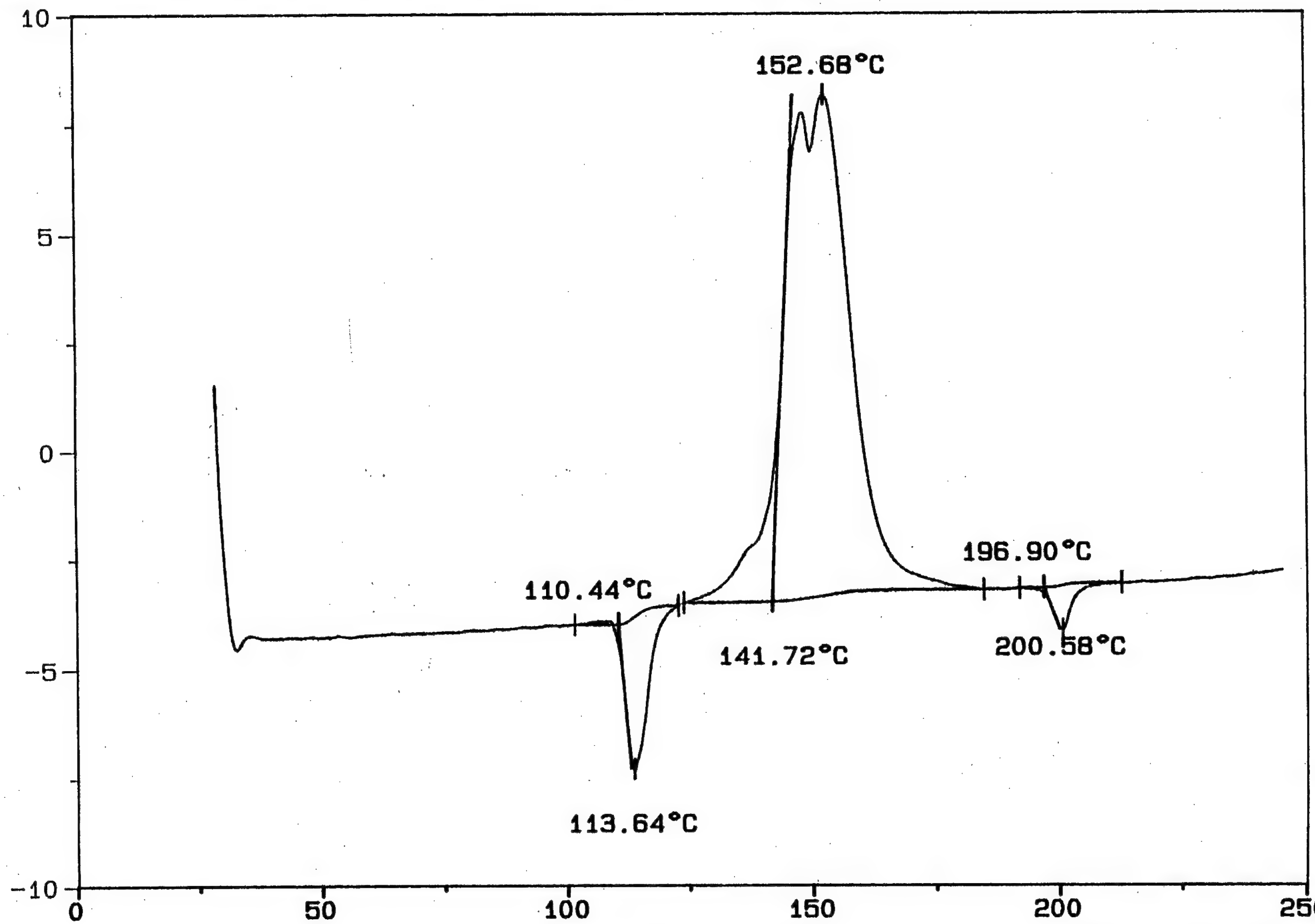
Metathesis:



Sample: DIMETHYLTRIAZANIUM CHLORIDE
Size: 1.0000 mg
Method: GREG
Comment: SEALED COATED AL PANS UNDER N2/50 ML/MIN N2

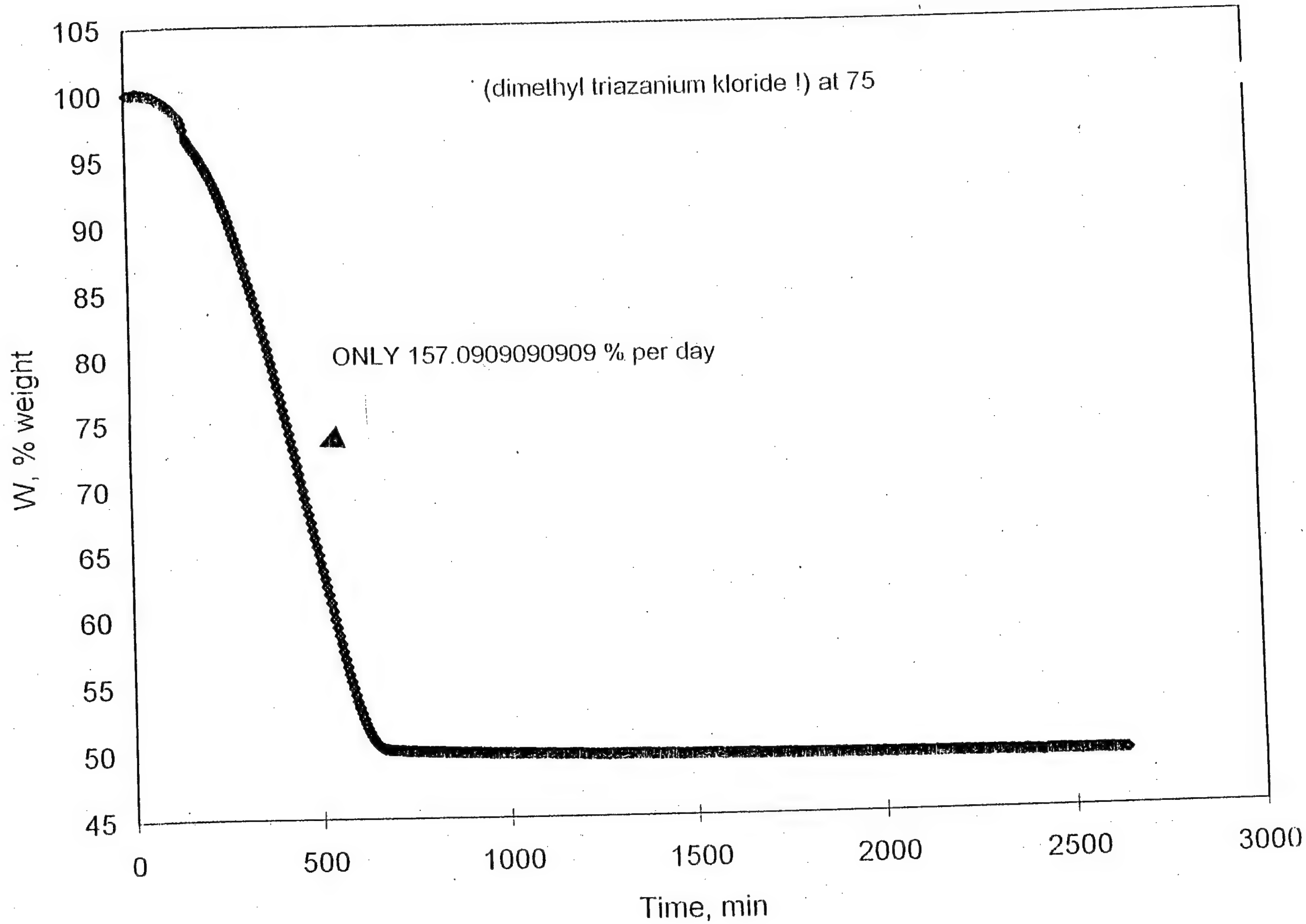
DSC

File: GWD.007
Operator: GREG DRAKE
Run Date: 10-Feb-99 19:12



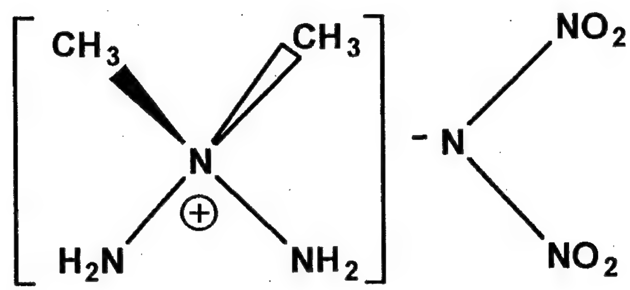
DSC V4.0B DuPont 2000

2/18/99



(dimethyl triazanium kloride !) at 75
ONLY 157.0909090909 % per day
W, % weight
105
100
95
90
85
80
75
70
65
60
55
50
45
0
500
1000
1500
2000
2500
3000
Time, min

Dimethyltriazanium dinitramide

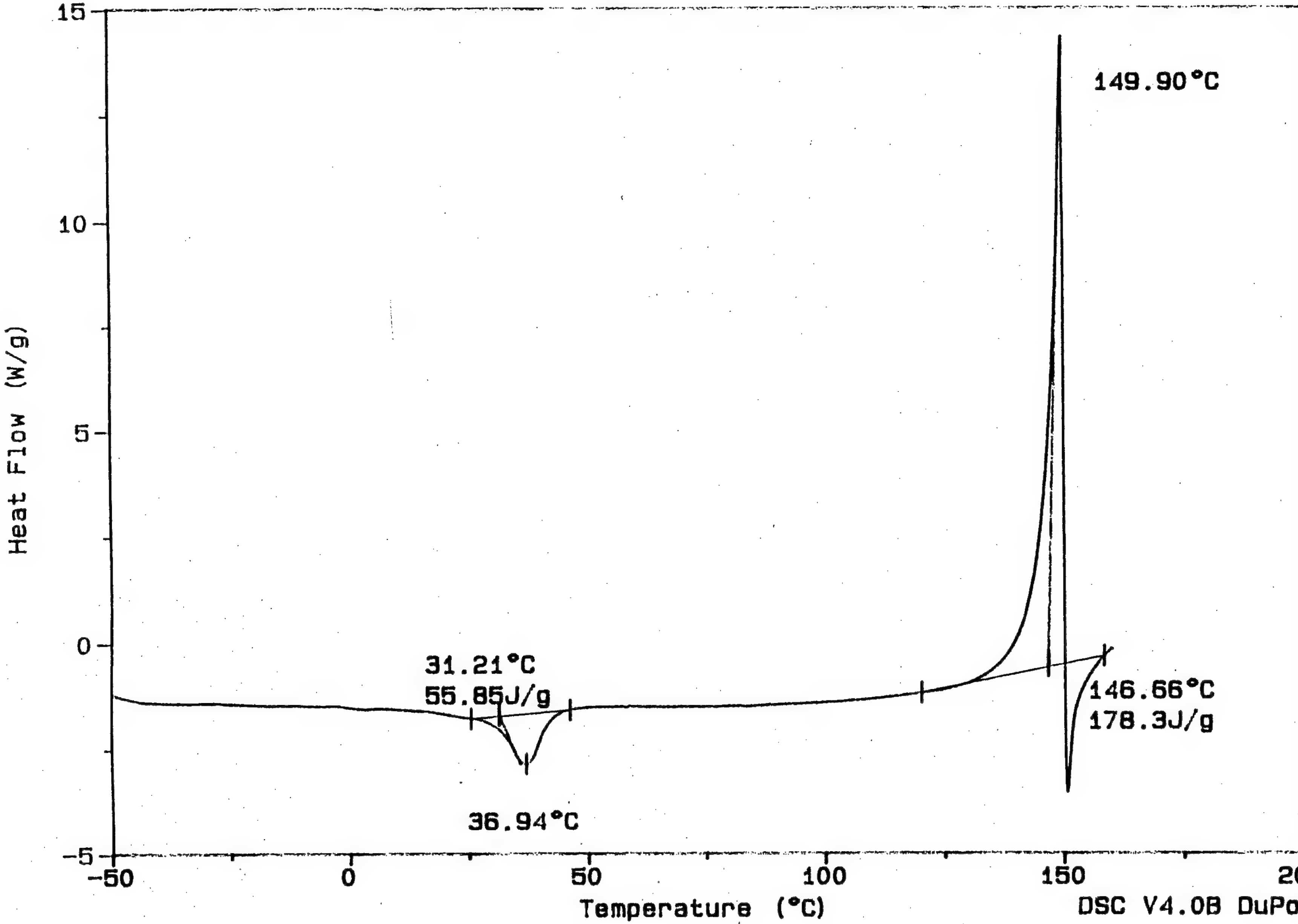


White crystalline solid
Melting point: 32°C
DSC: Surprising liquid range with major exotherm at 145°C
Impact: xxx kgcm
Friction: xxx newtons
Thermal stability at 75°C: xxxx

Sample: DMTDN CRYSTALS
Size: 1.7000 mg
Method: PROPELLANTS
Comment: 10°C/MIN, HERMETIC ALUM PANS, GN2 50ML/MIN, REPARED IN GLOVE BOX

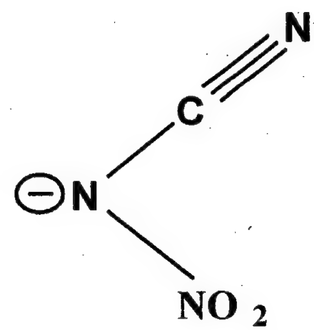
DSC

File: GD.009
Operator: GREG DRAKE
Run Date: 7-Mar-99 19:53

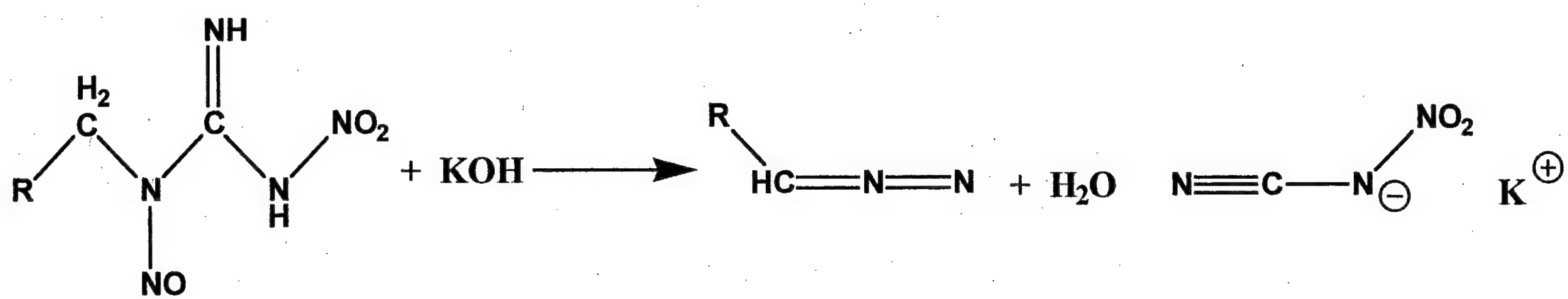


DSC V4.0B DuPont 2000

Energetic salts of the nitrocyanamide anion



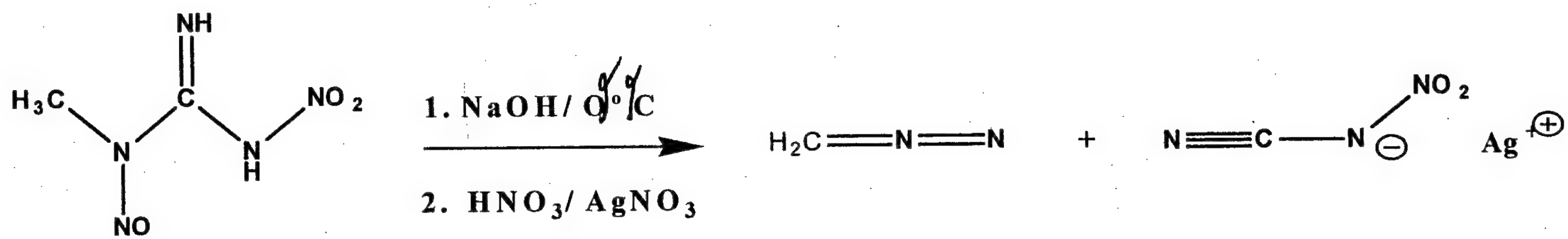
First isolated by McKay and coworkers[1] in 1950 as one of the products in the synthesis of diazohydrocarbons

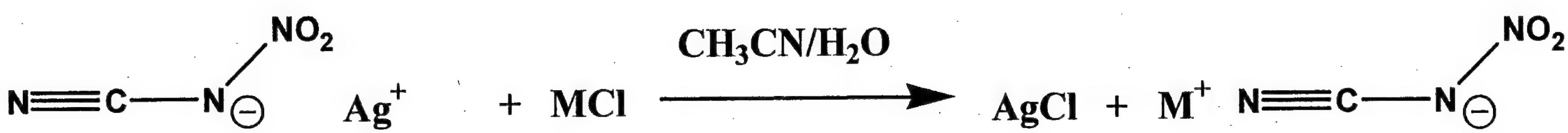


[1] Mckay, A. F.; Ott, W. L.; Taylor, G. W.; Buchanan, M. N.; Crooker, J. F. Can. J. Chem. 1950, 28B, 683.

In 1958, Sam Harris reported the synthesis and characterization of a large family of nitrocyanamide salts as new primary explosives/initiators as possible replacements of mercury fulminate.

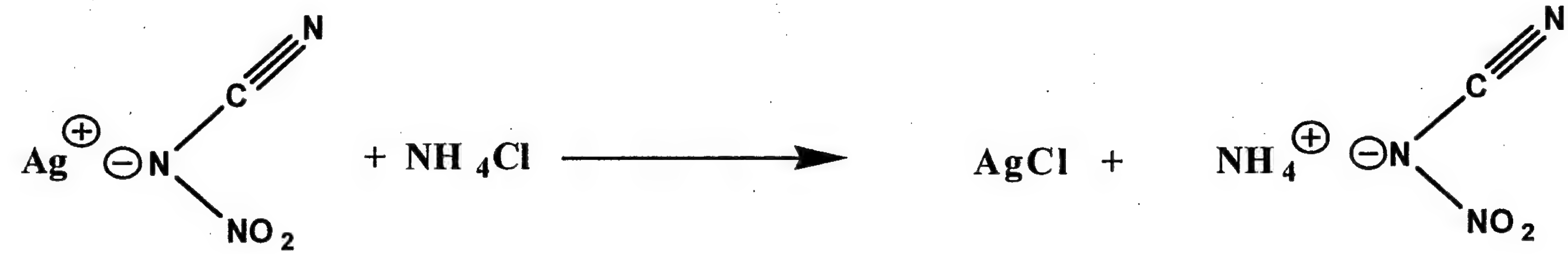
General reaction scheme:





Harris, S. J. Amer. Chem. Soc. 1958, *80*, 2302.

Ammonium Nitrocyanamide, $[NH_4][N(NO_2)(CN)]$



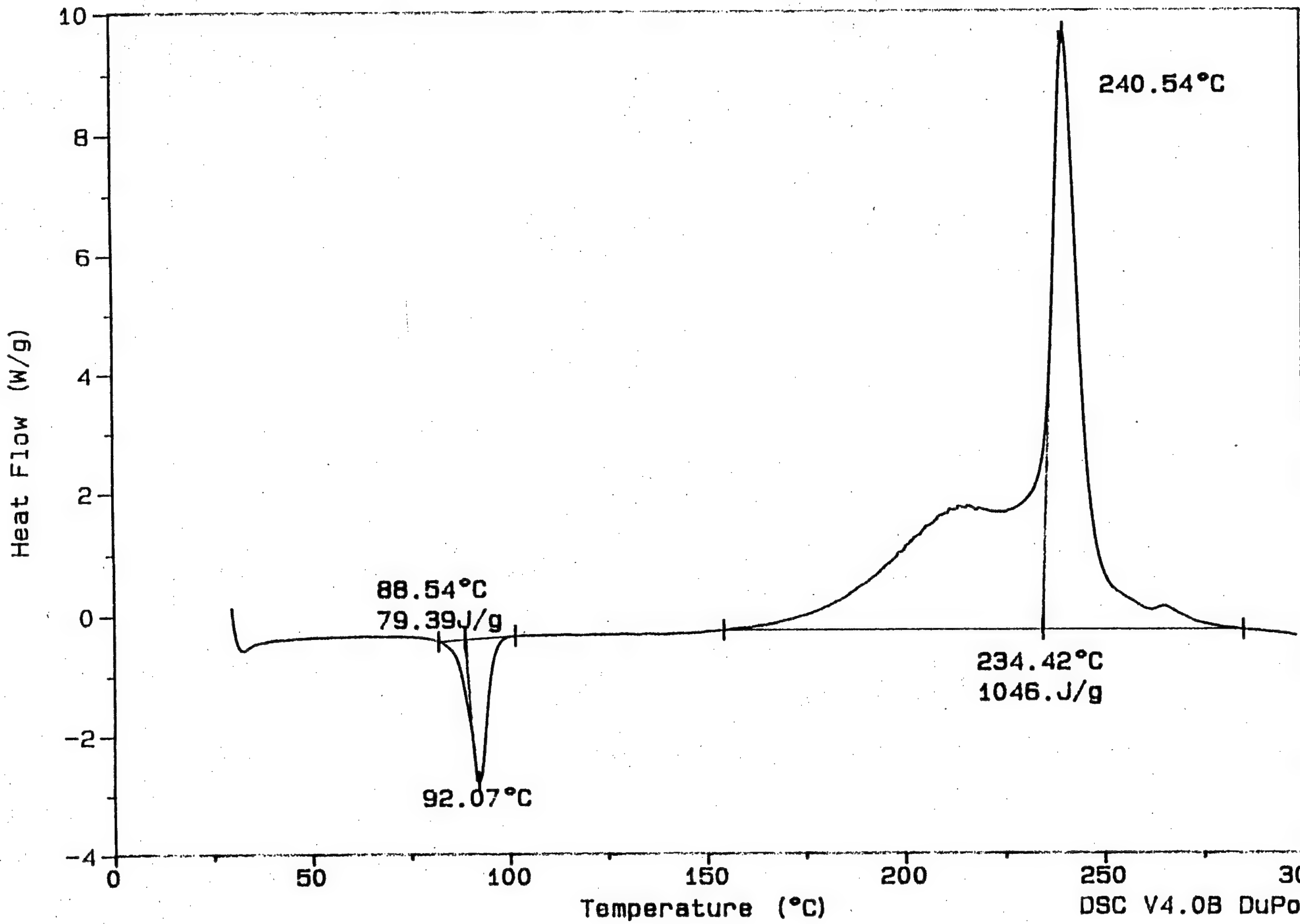
White powder
Melting point: 92°C*
DSC: slow exotherm beginning at 160°C
Impact sensitivity: impact insensitive at highest setting
200 kgcm (4 kg at 50 cm)
Friction sensitivity: insensitive at highest setting
37.8 kg (371 Newtons)
Thermal stability at 75°C: not very good at 3.8% per day

Harris, S. J. Amer. Chem. Soc. 1958, 80, 2302.

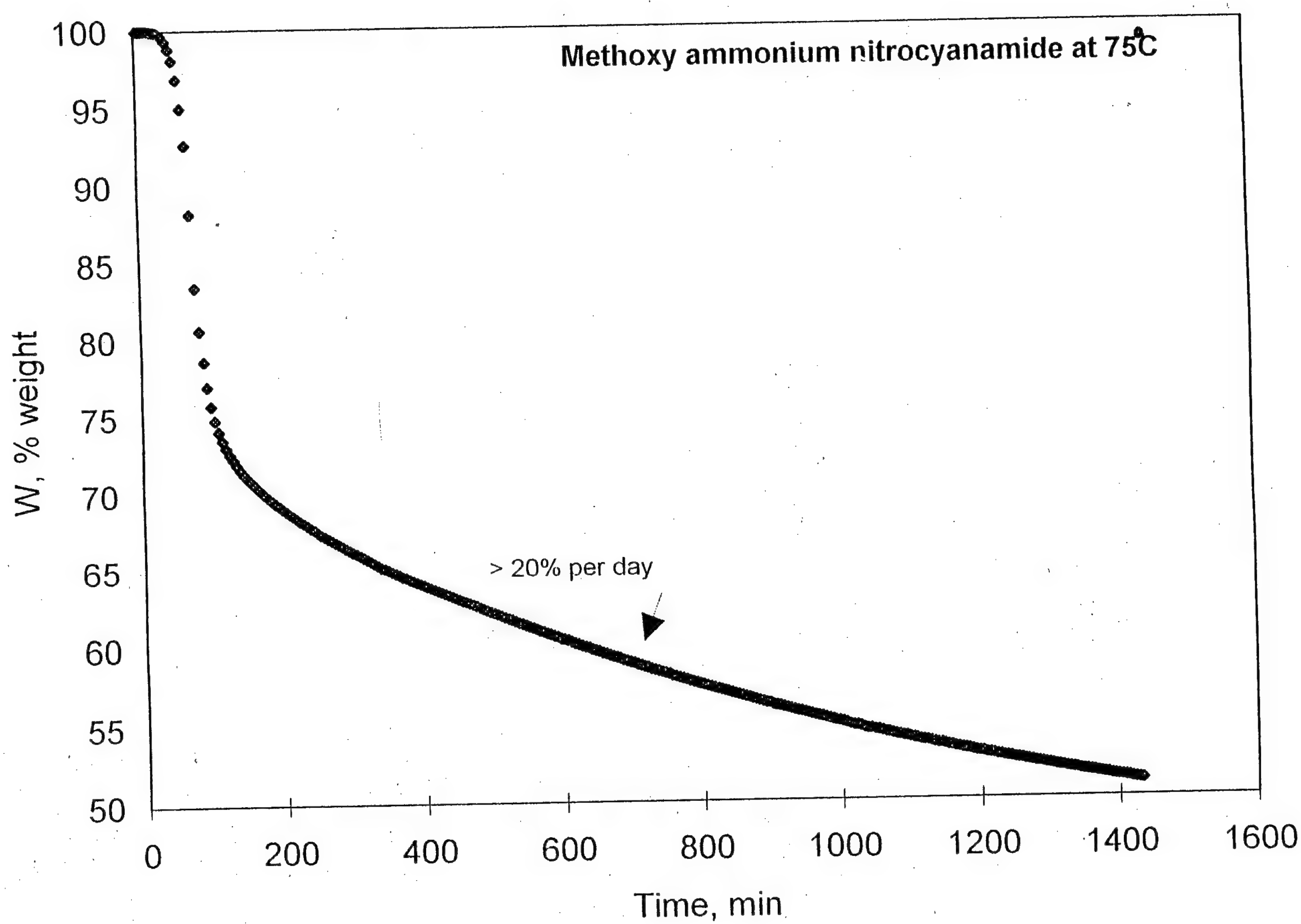
Sample: NH4N (NO2) (CN)
Size: 1.3000 mg
Method: PROPELLANTS
Comment: 10°C/MIN, HER AL PANS, GN2 50 ML/MIN

DSC

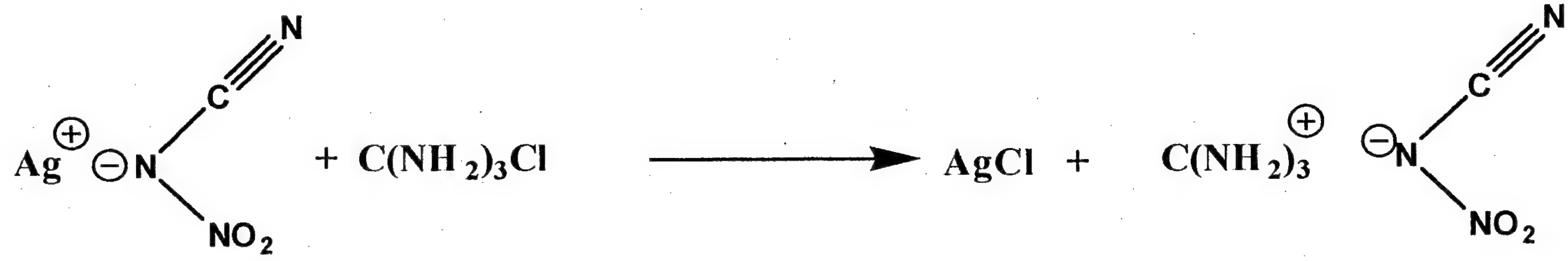
File: A: DRAKE.030
Operator: JONES/DRAKE
Run Date: 10-Feb-98 07: 24



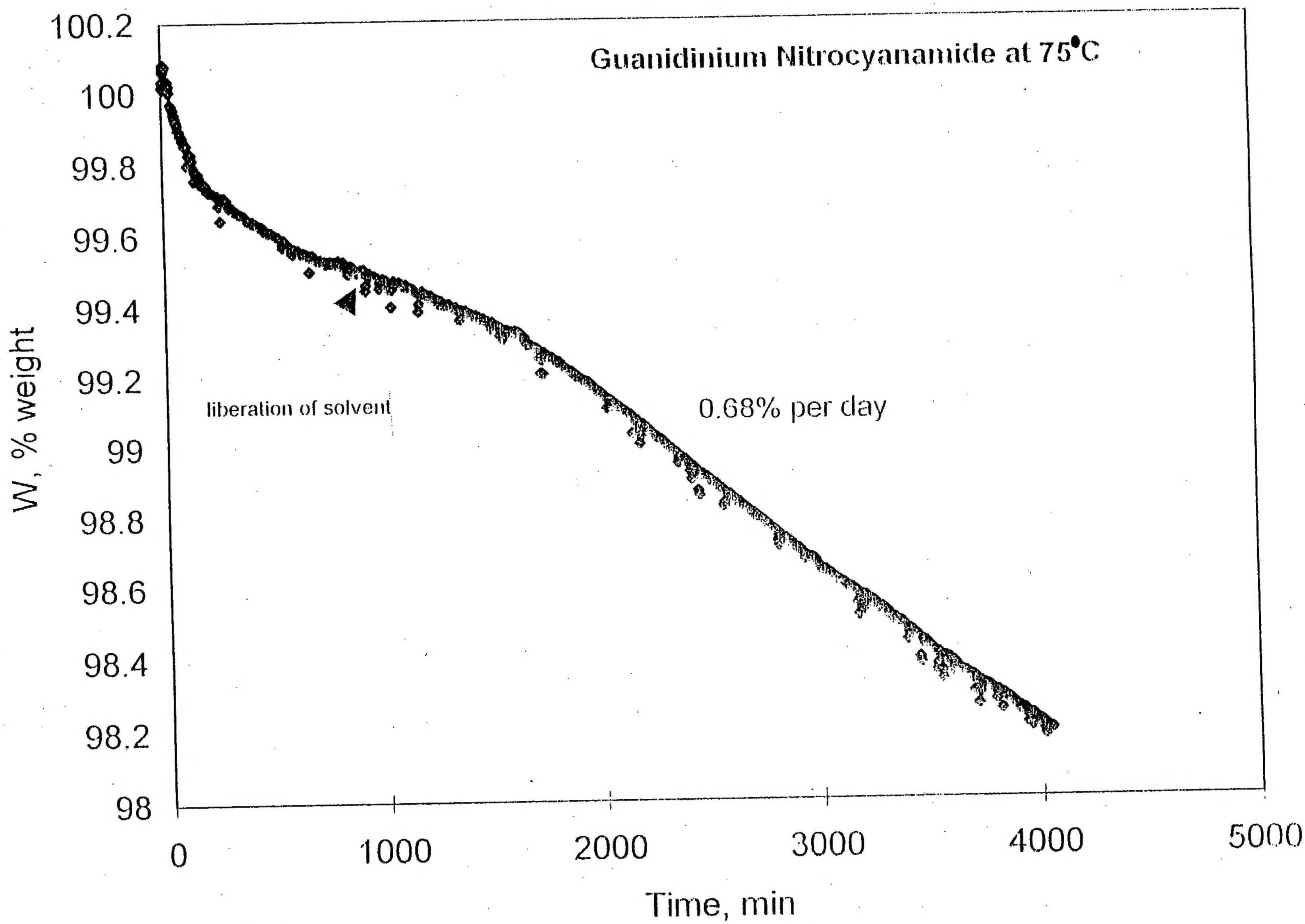
DSC V4.0B DuPont 2000


Methoxy ammonium nitrocyanamide at 75°C
> 20% per day
W, % weight
100
95
90
85
80
75
70
65
60
55
50
0
200
400
600
800
1000
1200
1400
1600
Time, min

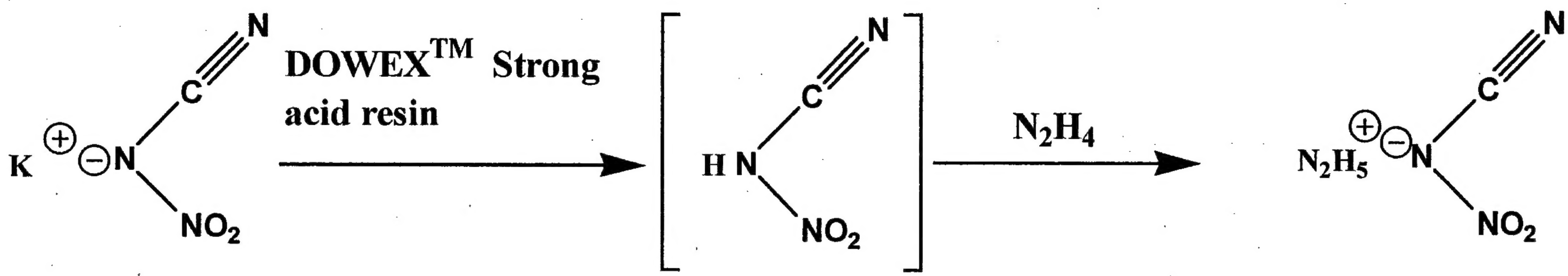
Guanidinium nitrocyanamide, $[C(NH_2)_3][N(NO_2)(CN)]$



White solid
Melting point: 131°C
DSC: melt with a large exotherm at 148°C
Impact sensitivity:
Friction sensitivity:
Thermal stability at 75°C: good passing at 0.64% loss/24 hours


Guanidinium Nitrocyanamide at 75°C
100.2
100
99.8
99.6
99.4
99.2
99
98.8
98.6
98.4
98.2
98
W, % weight
liberation of solvent
0.68% per day
0
1000
2000
3000
4000
5000
Time, min

Hydrazinium nitrocyanamide, $[N_2H_5][N(NO_2)(CN)]$



White, crystalline needles
Melting point: 89°C
DSC: complex decomposition with broad exotherms after melt
Impact sensitivity: 10 kgcm (5 negatives)
Friction sensitivity: 7.8 kg (77 newtons)
Thermal stability at 75°C: < 1% per day

Summary and Conclusions

2-hydroxyethylhydrazine makes an excellent starting material for a new set of energetic salts. The 1:1 salts of 2-hydroxyethylhydrazine have good physical properties, including good densities, liquids at ambient temperatures, and good thermal stabilities at elevated temperatures. These 1:1 salts pass the initial "tough" hurdles required for new candidates and look promising as replacements for hydrazine. The 1:2 salts are impact and friction sensitive, but they may have a future in high explosives work.

Dimethyltriazanium salts were reinvestigated and put through several tests. Although energetic, they have poor thermal stability at elevated temperatures and probably will not make good propellant ingredients.

Simple nitrocyanamide salts are energetic materials, which will require more work. Our initial work with small energetic cations (NH_4, N_2H_5, CH_3ONH_3), show that these salts are not very stable at elevated temperatures. But, larger cations, such as the guanidinium salt, appear to be more thermally stable, and more work will be put into investigating larger cation based salts.

Acknowledgements

United States Air Force (Funding)

Dr. Suresh Suri

Dr. Pat Carrick

Dr. Jeff Sheehy and Dr. Jerry Boatz

Dr. Steve Rodgers

Dr. Karl Christe and Dr. Bill Wilson

Mr. Paul Jones